INVESTIGATIONS

ON THE

TOLUIC, AND NITROTOLUIC ACIDS.

INAUGURAL DISSERTATION

FOR THE ATTAINMENT

OF THE

DEGREE OF DOCTOR OF NATURAL SCIENCES

AT THE

UNIVERSITY OF TÜBINGEN,

UNDER THE PRESIDENCY

OF

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PRESENTED

BY

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TÜBINGEN, 1872.

PRINTED BY L. FR. FUES.

In presenting this Dissertation to a highly-distinguished Faculty, as candidate for the degree of Doctor of Natural Sciences, I take the opportunity of conveying my thanks to Professor Fittig for having suggested the subject, and assisted in the work, described in this paper, and for his great kindness to me, during my stay at the University of Tübingen.

To determine the constitution of chemical compounds has been the endeavour of chemists, ever since the mere discovery of new bodies has ceased to engross their chief attention. And much labour has been expended on organic compounds, partly, perhaps, from the fact, that they form such a complete group by themselves, and have but few counterparts among inorganic compounds; and partly because they possess properties, which render their investigation comparatively easy.

When two or more bodies, having the same empirical formula and the same molecular weight, differ from each, other in physical properties, they are termed isomeric. This isomerism is explained by the theory that their component atoms have different relative positions. With regard to many of these isomeric bodies, it is known wherein they differ; this is usually acertained by the method of their formation, or by the products of their decomposition.

When two of the atoms of hydrogen in benzol are substituted by two monovalent atoms or groups, it has been found that three compounds are formed, all of which are isomeric. To account for this, the hypothesis has been advanced by KEKULÉ, that the isomerism of the three bodies is caused by the different relative positions of the substituting atoms in the benzol. The supposition that benzol is a ring of six atoms of carbon, united to each-

other alternately by single and double affinities, and each united by the remaining affinity to an atom of hydrogen, renders this hypothesis extremely probable. The proofs which are generally received, to affix determined positions to the substituting groups, or atoms are as follows:

According to the investigations of GRAEBE [1]), if pentachloro-naphthalene be oxidised with sulphuric acid, and manganic peroxide, an acid, belonging to the aromatic series of bodies is formed — viz., tetra-chloro-phthalic acid. The penta-chloro-naphthalene is formed from dichloro-naphthoquinone by the action of phosphoric chloride. Dichloro-naphthoquinone, gives, by oxidation with nitric acid, phthalic acid. If naphthalene be supposed to consist of two benzol rings with two atoms of carbon common to both, it is clear that in the one case, one of those rings must have been destroyed by oxidation, and in the other case, the other ring. If this be granted, the two carboxyle groups of phthalic acid must be situated next each other.

The proof of isophthalic acid, given by BAEYER [2]), is, that it has been obtained from mesitylene; in which, on account of its derivation from acetone, the three methyl groups are supposed to have the relative positions 1, 3. 5. Consequently the positions of the two carboxyle groups in isophthalic acid are 1, 3.

Since the position of the lateral groups of two of the isomeric compounds are in so far proved, there remains but one for those of terephthalic acid. — viz. 1, 4.

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1) Ann. der Chem. und Phar. CXLIX., p. 20.

2) Ann. der Chem. und Phar. Suppl. V. p. 79.

MEYER has given an additional proof of the constitution of salicylic acid [1]), from the following data: HÜBNER, and PETERMANN derived two isomeric bromo-amido-benzoic acids from a bromo-benzoic acid, which has been proved to contain the bromine and carboxyle situated with regard to eachother as 1, 3. Both of those give anthranilic acid, when the atom of bromine is removed by means of sodium. The reaction can be explained only by supposing, that the amido-group, and the carboxyle group have positions next to eachother. Anthranilic acid has been changed into salicylic acid, by HOFMANN [2]), by the action of nitrous acid.

That phthalic acid, and hydroquinone are also ortho-compounds, is made probable, by the fact that the former gives an anhydride, and the latter, quinone. It must necessarily be interesting to ascertain the relative places of the lateral groups of other di-substituted benzols, by transforming them, by means of suitable reactions, into any one of these three compounds, or into one, whose constitutional formula is already known, having been previonsly changed into *ortho*, meta, or *paraphthalic* acid.

It was for this purpose, that the work which this paper describes was undertaken. There has for a long time been a doubt of the proof of the *ortho* position of the two groups in salicylic acid; as the latter compound has been obtained by BARTH [3]), from potassic-orthotoluol-

1) Annal. der Chem. und Phar. CLVI, p. 295.
2) Annal. der Chem. und Phar. LXXV, p. 361.
3) Annal. der Chem. und Phar. CLII, p. 94.

sulphate by the action of fusing potassic-hydrate and the subsequent oxidation of the methyl group, it is evident that if the potassic-orthotoluol-sulphate can be submitted to such reactions as will bring it into nearer relation with phthalic acid, an additional proof is given, of this grouping of the entering *rests*.

This was attempted in the following manner.

Formation of toluic acid from toluidine.

Toluol was acted on with concentrated nitric acid, in order to procure nitrotoluol; ortho, and paranitrotoluol are formed. This was distilled with water vapour, and, after being dried over calcic chloride, fractionated ten, or fifteen times, to separate the ortho, from the para-nitrotoluol. Paranitrotoluol is a solid body crystallising in long needles, and boils at 236°; orthonitrotoluol is liquid and boils at 222—223°.

The latter was shaken with granulated tin, and hydrochloric acid, to change the nitro, into the amido group; a compound of orthotoluidinic chloride with stannic chloride is formed. This was distilled from a copper vessel with potassic hydrate, and the orthotoluidine, wich distils over with water vapour, collected in a receiver. It has the appearance of a heavy, transparent, oily liquid. A considerable portion was mixed with an equal weight of oxalic acid, and distilled at as high a temperature as possible. The reaction discovered by HOFMANN [1]), was expected to occur:

1) Ann. der Chem. und Phar. v. CXLII. p. 122.

$$\left.\begin{matrix}(C_2H_2)H\\H_2\end{matrix}\right\}O_2 + \left.\begin{matrix}C_7H_7\\H\\H\end{matrix}\right\}N = \left.\begin{matrix}CHO\\C_7H_7\\H\end{matrix}\right\}N + H_2O + CO_2.$$

$$\left.\begin{matrix}CHO\\C_7H_7\\H\end{matrix}\right\}N = C_8H_7\ N + H_2O.$$

The distillate, a yellow oil, was treated with concentrated hydrochloric acid, and again distilled. The residue in the retort was filtered off, dried between folds of filter-paper, and was a hard resinous mass. When dissolved in hot alcohol, in which it is extremely easily soluble, it crystallised out, on the alcohol cooling, in long white needles. It was got in a state of considerable purity by this means. It dissolves easily in ether, and appears to be insoluble in water. It may by easily sublimed, white crystals being obtained, which melt from 204°—206°. It was not, however, more closely investigated.

The distillate consisted of dilute hydrochloric acid with which a few drops of oil had distilled over. It was shaken up with ether, which was drawn off and distilled. The residue was boiled for some days with alcohol and potassic hydrate, to transform the cyanotoluol into toluic acid. The quantity obtained was too small, to admit of investigation. It melted irregularly about 145°, shewing it to be an impure compound. The process of resolving the amido compound into the cyanide does not succeed so well with toluol, as with its homologue benzol, probably on account of the greater complication in the constitution of the former substance; orthotoluidine,

also, possibly does not enter into this reaction so easily as its isomers para, or metatoluidine. A large quantity of carbon separated during the distillation with oxalic acid, and the chief product was the white substance already mentioned. The distillation was repeated several times with the same resulte, so the process was abandoned, in favour of the one which will now be described.

I.

Formation of Toluic acid, from Potassic Toluolsulphate.

Potassic toluolsulphate was prepared by the method given by ANNA WOLKOW [1]). Some pure toluol, boiling at 110° C. was added gradually to an equal quantity of fuming sulphuric acid, and the mixture shaken up, till complete combination took place. The acid was then neutralised with calcic carbonate and filtered. The small quantity of calcic sulphate dissolved in the filtrate was precipitated by adding a small quantity of baric hydrate, and the excess of the latter removed by passing carbonic acid through the liquid, as long as a precipitate continued to be formed. The calcic and baric carbonates, and the baric sulphate formed, were filtered off, and potassic carbonate added to the filtrate. Calcic carbonate, and potassic toluolsulphate were formed; the liquid was again submitted to filtration to remove the former. It was attempted to separate the ortho from the para-potassic-toluol sulphate; good crys-

1) Zeitschr. f. Chemie 1870. 321.

tals of the latter were obtained, but all attempts to get pure ortho salt were fruitless. The mixture of the two salts was evaporated to dryness, and kept for some days at a temperature of 100° C. in order to ensure absence of moisture. It was then intimately mixed with an equal weight of dry rowdered potassic cyanide, and distilled from an iron retort. The following reaction takes place.

$$C_7 H_7 SO_2 O K + KCN = C_7 H_7 CN + K_2 SO_3.$$

The cyanotoluol is a yellow, transparent, oily fluid, which does not mix with water. It was boiled with an alcoholic solution of potassic hydrate, for some days, till the ammonia formed, ceased to be evolved. The alcohol was then distilled off, and the residue shaken up with ether. On distilling off the etherial extract an oil was left behind, out of which some crystals of a solid white substance were obtained, by submitting it to a low temperature. The amount obtained was, however, not sufficient to induce investigation. Probably it was one of the products of distillation of potassic-toluol-sulphate alone, owing to its not having been thoroughly mixed with potassic cyanide. The residue, consisting of potassic toluate was boiled several times with animal charcoal, in order to remove the coloring-matter; it was then filtered, and the toluic acid precipitated by adding hydrochloric acid. The acid was collected, washed with a small quantity of cold water, and a calcium salt was formed by boiling it with excess of calcic carbonate. The acid which remained dissolved in the acid solution, was extracted with ether,

and was also neutralised with calcic carbonate. The solution of calcic toluate, having been filtered to get rid of the excess of calcic carbonate, was evaporated, till it became so concentrated, as to shew signs of crystallisation. A crystalline mass was obtained, which contained more para than ortho salt, as the latter is more easily soluble in water than the former. Great difficulty was experienced in obtaining a clear solution. No sooner was the boiling solution filtered, than it became again turbid. It was finally resolved to separate the different salts from one another by dissolving in water, and evaporating the solution till a scum was formed; then filtering and collecting the successive quantities of salt, which separated out and which were found to consist chiefly of calcic paratoluate. It was found possible to obtain considerable quantities of pure calcic paratoluate by this method, but for upwards of two months, attempts were made to obtain calcic orthotoluate, but in vain. After the two salts had reached a certain proportion, with regard to each other in the mixture, they appeared always to separate out in the same relative proportions. The attempt to separate the two salts by means of water, was accordingly given up; but the idea occurred that the separation might be successful, if the salts were crystallised from alcohol. This was done. The mixture, previously dried, and powdered, was dissolved in boiling alcohol, of 0.830 specific gravity. It dissolved with great ease, and on allowing the saturated solution to stand till it was cold, the calcic orthotoluate crystallised out in a state of con-

siderable purity. It was found, however, that when a small quantity of ortho, is mixed with a large quantity of para salt, the most advisable method is by boiling the crystalline mass obtained from a hot alcoholic solution on cooling, with an amount of alcohol insufficient to dissolve it. The calcic paratoluate is in great part dissolved, and the residue, consisting mainly of ortho salt, gives on crystallising from fresh alcohol, tolerably well defined crystals. It was only necessary to recrystallise them two or three times, to get a salt, which gave an acid of constant melting-point. The crystals obtained from the alcoholic solution have the appearance of radiating tufts of white needles. An analysis was made with the following results.

Analysis of Calcic orthotoluate.

0.2038 grm. lost on drying at 130°, 0.0209 = 10.26% H_2O

0.1829 grm. gave 0.0846 $CaSO_4$ = 13.05% Ca.

	Theory.	Found.
H_2O (2 mols.)	10.40%.	10.26%.
Ca	12.90%.	13.05%.

This confirms the statement of FITTIG and BIEBER [1]), that the calcic orthotoluate crystallises with two molecules of water.

Orthotoluic acid was precipitated from a solution of calcic orthotoluate by hydrochloric acid as a crystalline

1) Annal. der Chem. und Phar. CLVI, p. 243.

powder. The fusing-point was found to be exactly 102° C. It crystallised from a solution in hot water in long glancing needles, and possesses an aromatic odour.

Products of Oxidation of Orthotoluic acid.

About a gram of orthotoluic acid was put into a flask connected with a reversed condenser. A solution of three parts of potassic dichromate in five parts of sulphuric acid diluted with three times its volume of water was used. A set of potash bulbs, such as is used in organic analysis was filled with lime water, and connected with the end of the reversed condenser. The flask was heated over a sandbath, and no sooner had boiling commenced, than a gas was given off in great quantity; it was proved, by the immediate turbidity of the limewater, to be carbonic anhydride. A voluminous precipitate of calcic carbonate was soon thrown down; the evolution continued with great energy for about ten minutes, but did not entirely cease till an hour had elapsed. On the evolution of gas ceasing, the contents of the flask were diluted with some water, and shaken up with ether, which was drawn off with a pipette, and distilled. It left a scarcely perceptible residue, much too small for investigation.

It is thus conclusively proved that the substance on hand was pure orthotoluic acid, as FITTIG and BIEBER obtained the same results, by oxidation of the orthotoluic acid they obtained from orthoxylol. The acid obtained by them had exactly the same properties, owed the same

fusing-point, gave similarly formed crystals from an aqueous solution, and in short was identical with the acid obtained by me. A nitro-acid, melting at 145°, was made, which will be afterwards described, corresponding in its properties with that got by them.

We see, then, that orthotoluic acid may be obtained from one of the potassic toluolsulphates formed; but it remains to be shewn that no metatoluic acid is produced. Meta, and paratoluic acids have, in their salts, properties so very similar, as to render it a matter of extreme difficulty, if not of impossibility, to separate them, by crystallisation of any one of them. The lime, and the barium salts of the two acids crystallise together, presenting an appearance usually ascribed to a pure substance, viz., well-formed crystals, but on the melting-point being determined, an acid is obtained, which melts at a varying temperature. So it was not attempted to separate the two acids (if both were present) by this process. The same result would be obtained, if the residue, after gaining as much orthotoluic acid as possible, were oxidised, as the orthotoluic acid would be completely destroyed by oxidation, forming carbonic acid, and water, and the meta, and paratoluic acids would yield respectively iso, and terephthalic acids. The two latter are neither difficult to separate from each other, nor to identify in presence of each other.

Products of Oxidation of the Residue.

The solution, after a considerable quantity of paratoluic acid had been obtained from it, was acidified with hydrochloric acid to precipitate the mixture of toluic acids, which were then oxidised in the same manner as was the orthotoluic acid, by boiling for some days with potassic dichromate, and dilute sulphuric acid, with a reversed LIEBIG'S condenser, on a sandbath. An insoluble substance separated ont; it was found however that the acids, produced by oxidation combined with the chromium probably to form a salt. This was, however, easily decomposed by boiling with potassic carbonate, and the acids, procured by precipitation, were collected, and distilled for some days with boiling water, to ensure that no paratoluic acid, which might not have been oxidised, was present. The residue was boiled with a fresh portion of water, and filtered off. The insoluble portion must consist chiefly, if not entirely of terephthalic acid; but as that is known to dissolve, though with difficulty, when other acids are present in any quantity, the filtrate was boiled with baric carbonate to form a barium salt of the acids. The solution of the salt was evaporated, and the successive portions of baric terephthalate removed as they deposited as a scum on the surface. When as much as possible had been removed, the remainder was set aside to see if crystals would deposit. No crystals were observed, but the acid was again precipitated, and again distilled

with water-vapour. A very small quantity of undecomposed toluic acid was observed to distil over, which had probably been the cause of the solubility of the terephthalic acid. The acid remaining in the flask was apparently insoluble in water, and when again boiled with baric carbonate, the resulting salt was not crystalline, and could not be obtained in crystals. It may be concluded then, that it is extremely improbable that isotoluic acid is present; if it is, it must be in such small quantity as to make identification by means of oxidation impossible.

It will be shewn that the paratoluic acid, obtained from the mixture of calcic ortho and paratoluate contained no metatoluic acid; a nitro-acid having been made from it, which proved to be identical with that of AHRENS [1]).

It is thus seen, that orthotoluic acid has been obtained from potassic-orthotoluolsulphate, and as the latter substance has been resolved into salicylic acid we have thus a connecting link between the two acids. Salicylic acid is, accordingly, ortho-oxybenzoic acid, and ortho-toluic acid, ortho-methylbenzoic acid.

BEILSTEIN and KUHLBERG [2]), assert that they obtained salicylic acid from cinnamic acid and assign on that ground the meta position to its „rests". This research contradicts their statement and gives, besides, another indirect proof of the constitution of compounds such as anthranilic acid, of ortho bromo, chloro, and iodo-benzoic acids, for,

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1) Zeitschr. für Chem. 1869. p. 104.

2) Ann. der Chemie und Physik.

these acids are all connected with salicylic acid, either by giving the latter, when submitted to suitable reactions, or by being produced from them. It also confirms the neatness of the well known reaction — distilling a sulphoacid with cyanides — on which some doubts have been thrown as to the possibility of the existence of an orthocyano-compound. Although the yield of cyanotoluoflid not bear a large proportion to the amount of potassic toluolsulphate employed, still a sufficient quantity was obtained, to show that it was the chief product of distillation.

Metatoluic acid.

Metatoluic acid, although it has been obtained by several chemists has, as far as I am able to find out, never been obtained in sufficient quantity and purity to admit of investigation. AHRENS [1]) obtained it from bromo-metatoluic acid, by removing the bromine with sodium. RICHTER [2]) also obtained it from bromo-nitro-toluol by heating it with potassic cyanide in alcoholic solution and by subsequent debrominating. The former states that the acid he obtained fused at 90°—93° C. The latter gives as the fusing-point of his acid 105—106° C.

WURTZ [3]) mentions, that from bromotoluol and chlorocarbonic ether, he gets a toluic ether, the acid extracted

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1) Zeitschr. für Chem. 1869. p. 104.

2) Berichte der Deutschen chem. Gesellschaft V. 426.

3) Comptes Rendus pour 1870. p. 350.

from which melts at 153°. He succeeds in resolving this, which is a mixture, into two acids, — one melting at 176° —77°, — undoubtedly paratoluic acid, — and one melting at 90°, which he characterises as identical with that obtained by AHRENS. And, lastly, in support of RICHTERS statement, an acid has been lately obtained in the laboratory at Tübingen, the formation of which prohibits the possibility of an admixture of isomeric acids, without a rearrangement of molecules, which also fuses at 105°.

As metatoluic acid is a not uncommon product of oxidation of toluol-compounds, it was thought of interest to determine which of these statements is correct. It is a generally observed rule also, that the fusing-points of the three isomeric acids increase in the order of ortho, meta, and para. Thus in the phthalic acid row, phthalic acid melts at 182°; isophthalic acid, at above 300°, and terephthalic acid does not melt. The toluic acids, provided the meta-acid melt as stated by AHRENS, at 90—93° forms an exception to this rule, as the melting-point of the ortho, as given by FITTIG is 102° C. and that of the para, 176—77.

In the preparation of metatoluic acid, the process of AHRENS was followed. A quantity of pure xylol, was submitted to the action of a fine stream of bromine for about three hours, being kept cool while the action was proceding, to ensure that the bromine should substitute in the benzol and not in the methyl rest. The bromine was added in the proportion of 160, to 106, and was absorbed with solution of a large quantity of hydrobromic

acid. As soon as the action ceased, the fluid was shaken up with sodic hydrate to remove any bromine which might not have been absorbed.

The watery solution was then removed, and the oily liquid shaken up several times with water, to remove the traces of sodic hydrate. It was ther left standing several days in contact with fused calcic chloride, by which all water was removed. The calcic chloride wastaken out; the liquid distilled, and the portion which came over between 205°, and 212° C., collected. This was a yellowish oil with a pleasant etherial odour. It was oxidised in portions of about five grams at a time by being boiled, for three days, in a flask with an inverted condensor, with a mixture of two parts of potassic dichromate, and three parts of sulphuric acid, diluted with three times its volume of water. A compound of a buttery consistence was obtained, which was found to contain chromium, and bromo-toluic acid, probably inclosed in a film of undecomposed bromo-xylol. This was decomposed by being boiled repeatedly, alternatety with a solution of a potassic carbonate, and hydrochloric acid. The potassic carbonate removes a portion of the bromotoluic acid in the form of a salt, from which the acid may easily be precipitated; while the hydrochloric acid dissolves the liberated chromic sesquioxide. The bromo-toluic acid is a white bulky precipitate. At least two bromo-toluic acids are formed, but presumably more. AHRENS found and investigated one, and by removing the bromine, obtained metatoluic acid. In order to separate the acid, from which metatoluic acid can be obtained, the calcium salt

was made by boiling the bromotoluic acid with calcic carbonate. The salts formed are soluble in water but one of them is soluble only with extreme difficulty. It was obtained only on boiling the residue, consisting of excess of calcic carbonate mixed with the calcium salt, repeatedly with water; on filtering off, the salt crystallised out of the filtrate, almost immediately, on slightly cooling. It presents the appearance of long, transparent needles, and, on account of its comparative insolubility may be obtained pretty pure by recrystallisation a few times from water. „Pretty pure", for the sequel will shew that it has probably never been obtained perfectly pure. The acid, on being precipitated from this salt, gave a fusing-point of 205—207° C.

The whole of the bromotoluic acid of this fusing-point, was treated with nascent hydrogen, by means of sodium amalgam, for some days to remove the bromine. The action proceeds very easily; as soon it ceases, the liquid is freed from the mercury, and after being acidified with sulphuric acid, distilled. The metatoluic acid is liberated from its sodic salt, and distils over with the water vapour. A peculiarity, which was observed in distilling, is, that the acid has a much less tendency to solidify in distillation, and the aqueous solution has a strong smell. The distillate was neutralised with sodic carbonate, and evaporated to a small bulk, from which the acid was precipitated. It is more easily soluble in water than its isomers. It can be obtained in long needles, by cooling its aqueous solution. The acid obtained melted at 90—91°.

It was accordingly thought, that the statement of AHRENS was correct, and an analysis of the barium, and calcium salts were undertaken

Calcic metatoluate $\left(C_6 H_4 \begin{cases} C H_3 \\ C O O \end{cases}\right)^2 Ca.$

Calcic metatoluate was obtained by the usual method of boiling the acid, in aqueous solution, with calcic carbonate and crystallising the resulting salt. It presents the appearance of calcic orthotoluate, when crystallised from alcohol, viz. radiating tufts of white needles. They appear to lose water over sulphuric acid; the amount taken for analysis was, accordingly, dried in the air.

Analysis.

0.2056 grm. lost on drying at 140—50° 0.0291 = 14.15% $H_2 O$.

0.1765 grm. gave 0.0776 grm. $Ca SO_4$ = 12.91% Ca.

Theory.		Found.
$H_2 O$ (3 mols)	14.86%.	14.15%
Ca	12.90%.	12.91%

Baric metatoluate $\left(C_6 H_4 \begin{cases} C H_3 \\ C O O \end{cases}\right)^2 Ba.$

Baric metatoluate was made by boiling with baric carbonate. It crystallised in small glancing plates. After standing over sulphuric acid for some days, it was dried at 150°. It is easily soluble in water.

Analysis.

0.2169 grm. lost on drying at 150°. 0.0172 = 7.92% H_2O.

0.1988 grm. gave 0.1132 grm. $BaSO_4$ = 33. 4% Ba.

Theory.		Found.
H_2O (2 mols)	8.12%	7.92%
Ba	33.6%	33.4%.

After having made these analyses, the acid was crystallised out of alcohol; and it was observed with great surprise, that two different kinds of crystals were formed which could easily be separated from each other. The one presented the apearance of large crystalline masses; the others of small warts. On crystallising them both separately out of fresh alcohol, the former melted at 105—106°; the latter however, at 176°. The latter is undoubtedly para, and the former metatoluic acid. The number 105° agrees with the melting point found by RICHTER, and is undoubtedly the right one. We must conclude that the bromo metatoluic acid has never been obtained in a state of absolute purity. Small traces of bromoparatoluic acid must have abhered to it throughout. The meta, and paratoluic acids appear to crystallise in the same form in their salts, and from this, arises the difficulty of separation. It was attempted to sublime the metatoluic acid, but owing to its low solidifying point it was not obtained in distinct crystals but in crystalline masses.

Metatoluic acid appears to crystallise from alcohol in monoclinic prisms.

As I was in possession of a considerable quantity of the toluic acids, it occurred to me, that it would be advantageous to make the nitro-acids, in order to investigate them comparatively. The three acids were, accordingly, prepared, and as the process was identical with each, it will be necessary to describe it only once.

The acid, precipitated from one of its well crystallised salts, usually the calcium one, was dried between folds of filter paper, and boiled with concentrated fuming nitric acid, till it thoroughly dissolved. The solution was then allowed to cool, and on cooling, the acid crystallised out, almost entirely, from the concentrated acid, and could be collected, and recrystallised out of alcohol.

Nitro-orthotoluic acid.

Nitro-orthotoluic acid crystallises in needles, which fuse at 145°. It is slightly soluble in water. On acting on orthotoluic acid, with nitric acid, only one acid is formed. The calcium salt was made with calcic carbonate, and analysed.

Analysis of calcic nitro-orthotoluate $\left(C_6H_3\begin{cases}C\,H_3\\C\,O\,O\\N\,O_2\end{cases}\right)^2 Ca$

0.1095 grm. lost on drying at 150°, 0.0093 = 8.49% H_2O.

0.1002 grm. gave 0.0349 grm. $CaSO_4$ = 10.26% Ca.

Theory.	Found.
H_2O (2 mols) 8.25%	8.49%
Ca 10.00%	10.26%

Nitro-meta-toluic acid.

Metatoluic acid was treated with nitric acid, and the solution deposited on standing, long needles. These were crystallised from alcohol, and it was plainly observable that two sorts of crystals were present. One kind was crystallised in long needles; the other in solid masses. It was not found possible to separate the two different acids. The mixture melted at about 217° C. AHRENS describes an acid, obtained from a mixture, whose melting point was 175°, which he resolved into two; one which melted at 220°, and had the appearance of monoclinic prisms; and one which crystallised in long needles, and melted at 217—18°. The acid obtained by me is evidently this mixture. As four separate acids, may be formed by the substitution of an atom of hydrogen, by the nitro-group, it is not to be expected that only one acid should be formed. A determination of the barium, in the salt of mixed acids, was made, with a view simply to determine the actual presence of nitro-metatoluic acid.

0.1445 grm. gave 0.0679 grm. $BaSO_4$ = 27.61% Ba.

Theory. 27.56% Ba.

Nitroparatoluic acid.

Paratoluic acid, melting at 176° C. was dissolved in fuming nitric acid. Tolerably well defined crystals were

obtained on the solution cooling; the nitric acid solution was poured off, and the crystals dissolved in alcohol. On adding water to the liquid from which the crystals had been obtained, a very small precipitate came down, showing that almost all the acid was deposited from the solution in nitric acid, on cooling.

The nitroparatoluic acid, crystallised from alcohol in large wel-formed, crystals (possibly rhombohedra), of a pale yellow colour. The fusing point was determined, and found to be 188°. Crystallised out of water, it presents the appearance of long, white needles, which have the same fusing-point.

Baric nitroparatoluate $\left(C_6H_3\begin{cases}CH_2\\COO\\NO_3\end{cases}\right)^2 Ba.$

Baric nitroparatoluate was obtained in the usual way, — by boiling the acid with baric carbonate, suspended in water. It is a white crystalline body, crystallising in tufts of fine needles; it is tolerably soluble in water from which it deposits as crystals when a hot solution cool.

Analysis.

0.4780 grm. lost, on drying at 150° — 0.0587 = 12.26% H_2O.

0.4193 grm. gave 0.1971 grm. of $BaSO_4$ = 27Ba. 0.6%

	Theory.	Found.
H_2O (4 mols)	12.65	12.26
Ba	27.56	27.60.

On consulting the literature, which treats of the ni-

trotoluic acids, we find that FITTIG [1]), obtained a nitro-orthotoluic acid, which melted at 145° by acting on orthotoluic acid with nitric acid. The acid obtained by me was identical with this one. It was not attempted to determine the position of the nitro-group. Four acids of this composition are possible, but as only one is formed, the carboxyl-group must determine the entering place of the nitro-group.

Metatoluic acid, on the other hand, when acted on by nitric acid yields two substitution products, which are not easy to separate from each other. It may be stated that the barium salt of which the analysis is given, was well crystallised in tufts of needles, and looked like a pure salt, but the acid, when precipitated from it did not shew a constant fusing-point.

NOAD [2]) was the first to describe a nitrotoluic acid; the one he obtained, by the action of weak nitric acid on cymol, must have been *para*, as the description which he gives of it coincides, that obtained from the paratoluic acid. AHRENS also made a nitro paratoluic acid, and gives the fusing-point 190°. The acid which I obtained, melted at 188°. Two acids are possible, but, as in the case of the ortho-acid, only one is formed.

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1) Annalen der Chemie und Pharm. CLVI. p. 244.

2) Phil. Mag. XXXII. 15; and Chem. Soc. Mem. III, 421.